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ELECTROCHEMISTRY OF SULFUR DIOXIDE IN NONAQUEOUS SOLUTIONS, PAR--ETC(U)  
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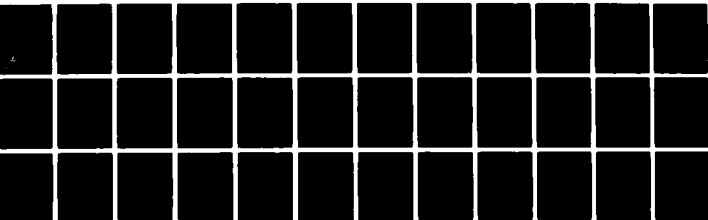
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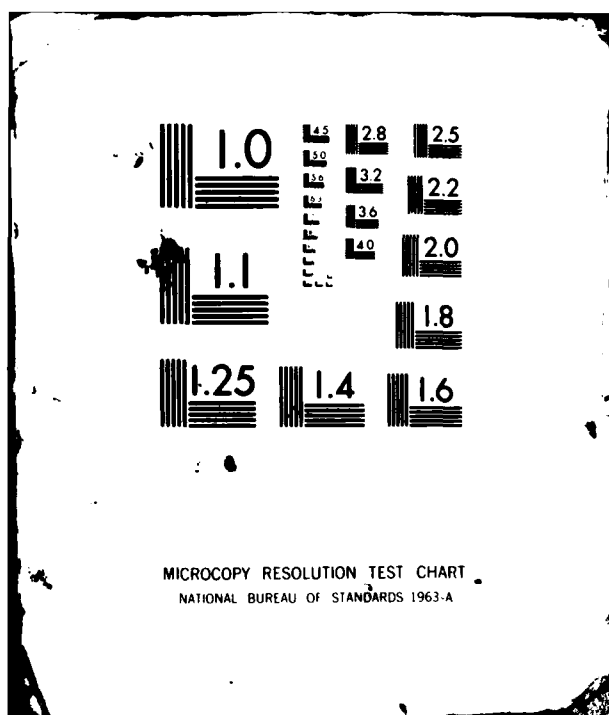
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# ELECTROCHEMISTRY OF SULFUR DIOXIDE IN NONAQUEOUS SOLUTIONS, PART 1

BY LINDA S. LAUGHLIN

RESEARCH AND TECHNOLOGY DEPARTMENT

18 MAY 1981

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## Chapter 1

## INTRODUCTION

Considerable interest in the electrochemical behavior of nonaqueous solutions of sulfur dioxide has been generated by the use of these systems in high energy density lithium batteries. During the past twenty years,  $\text{SO}_2$  in solvents such as dimethylformamide (DMF) and dimethylsulfoxide (DMSO) has been extensively studied. Only since 1978 have reports been appearing on actual battery solvents, propylene carbonate (PC) and acetonitrile (AN).

The reduction of  $\text{SO}_2$  has been studied by a variety of techniques, including ultraviolet (UV) and raman spectroscopy, electron spin resonance (ESR or EPR), controlled potential electrolysis, coulometry, chronopotentiometry, voltammetry and chemical reduction. There has been little consistency as to solvent, supporting electrolyte, working electrode surface or reference electrode, resulting in a patchwork of data. Published reports have been summarized in Table 1.

Whether the electron is transferred chemically or electrochemically, the first product is  $\text{SO}_2^-$ . Controversy begins over subsequent chemical processes, proposed to be either



or



Voltammetric and spectroscopic data have been interpreted to support one or the other pathway. Only recently have the many contributing factors been investigated. A review of the various studies should prove useful in the planning of future work. These have been grouped into cyclic voltammetric studies, Table 2, and other voltammetric studies, Table 3.

The experimental work performed in this laboratory will be presented in Part II of this report.



## Chapter 2

## DIMETHYLFORMAMIDE (DMF)

I. CHEMICAL REDUCTION

Rinker and Lynn reduced  $\text{SO}_2$  in several solvents, using sodium amalgam as the reductant, producing several species.<sup>1</sup> A blue radical ion obtained in DMF was identified as  $\text{SO}_2\text{SO}_2^-(x=1)$ , as well as a white precipitate which was primarily sodium dithionite,  $\text{Na}_2\text{S}_2\text{O}_4$ .

II. ELECTROCHEMICAL INVESTIGATIONA. TETRAALKYLAMMONIUM SALTS.

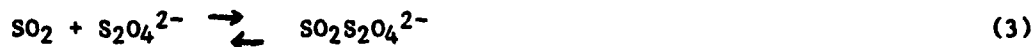
1. Platinum Electrode. Dinse and Mobius electrolytically generated  $\text{SO}_2^-$  in DMF-TPAP (tetrapropylammonium perchlorate) solution, studying the resulting species by EPR and UV spectroscopy.<sup>2</sup> From analysis of the changes in the EPR spectra with temperature, it was determined that for the complex,  $(\text{SO}_2)_x\text{SO}_2^-$ ,  $x=2$  and the formation constant is  $1.3 \times 10^4 \text{ M}^{-2}$  at  $0^\circ\text{C}$ . A blue-green color was observed at higher  $\text{SO}_2$  concentrations.

Martin and Sawyer found not only a blue species in DMF-TEAP (tetraethylammonium perchlorate), but a red species as well.<sup>3</sup> When  $\text{NaClO}_4$  was added to a completely electrolysed solution of  $\text{SO}_2$ , sodium dithionite precipitated. Cyclic voltammetry resulted in four peaks, two cathodic and two anodic. UV spectroscopy revealed two peaks, at 485nm and 580nm. One electron reduction of  $\text{SO}_2$  occurred at  $-0.85\text{V}$  (vs. SCE), with the corresponding oxidation of  $\text{SO}_2^-$  at  $-0.74\text{V}$ . The UV absorption at 580nm was identified with the blue complex,  $(\text{SO}_2)_x\text{SO}_2^-$ , which was oxidized at  $-0.24\text{V}$ . The red complex,  $\text{SO}_2\text{S}_2\text{O}_4^{2-}$ , absorbed at 485nm and was reduced at  $-1.65\text{V}$ . The absorption at 350nm of a completely electrolysed solution of  $\text{SO}_2$  was attributed to the presence of dithionite ion,  $\text{S}_2\text{O}_4^{2-}$ . The equilibrium constants were calculated to be  $24 \text{ M}^{-1}$  for eqn. 2 and 10 for eqn. 3.

<sup>1</sup>Rinker, R. G. and Lynn, S., "Formation of Sodium Dithionite from Sodium Amalgam and Sulfur Dioxide in Nonaqueous Media," Industrial and Engineering Chemistry: Product Research and Development, Vol. 8, 1969, pp. 338-347.

<sup>2</sup>Dinse, K. P. and Mobius, K., "EPR - Untersuchungen an elektrolytisch erzeugtem  $\text{SO}_2^-$ ," Zeitschrift für Naturforsch. A, Vol. 23, 1968, pp. 695-702.

<sup>3</sup>Martin, R. P. and Sawyer, D. T., "Electrochemical Reduction of Sulfur Dioxide in Dimethylformamide," Inorganic Chemistry, Vol. 11, 1972, pp. 2644-2647.



Magno, Mazzochin and Bontempelli found that  $\text{SO}_2$  was reduced at  $-0.95\text{V}$  (vs. aq. SCE) in DMF-TBAP (tetrabutylammonium perchlorate),<sup>4</sup> resulting in anodic peaks at  $-0.65\text{V}$  and  $+0.1\text{V}$ . The first peak was attributed to the oxidation of  $\text{SO}_2^-$  resulting from the dissociation of dithionite and the second peak to the direct oxidation of dithionite itself. The blue solution absorbed at  $580\text{nm}$  and analysis of the spectra indicated that the complex,  $(\text{SO}_2)_x\text{SO}_2^-$ , was formed. No correlation was observed between the peak at  $580\text{nm}$  and any voltammetric peaks. Coulometry showed that  $\text{SO}_2$  and the blue complex were both reduced at the  $\text{SO}_2$  reduction potential. The absorption spectra were interpreted to suggest that  $x > 1$ , probably equal to 2.  $\text{SO}_2$  absorbed at  $275\text{nm}$  and a saturated solution of  $\text{Na}_2\text{S}_2\text{O}_4$  at  $297\text{nm}$ . Completely reduced solutions of  $\text{SO}_2$  also absorbed at  $297\text{nm}$ . The positive shift of the anodic peak potentials and the increase in the second anodic peak at lower temperatures were assumed to result from weak adsorption of dithionite onto the platinum surface.

Kastening and Gostisa-Mihelcic investigated complex formation in DMF-TEABr (tetraethylammonium bromide) by ESR in order to determine the correct value of  $x$ .<sup>5</sup>  $\text{SO}_2$  was partially electrolysed and the ratio of the two radical species determined, leading to the conclusion that  $x=1$  and the equilibrium constant for complex formation (eqn. 1) is  $230\text{ M}^{-1}$ . The spectral data reported by Dinse and Mobius were recalculated for  $x=1$  (rather than 2)<sup>2</sup> and  $K$  was found to be  $65\text{--}200\text{ M}^{-1}$ , depending on  $\text{SO}_2$  concentration.

Bowden and Dey found two anodic peaks in the cyclic voltammograms of  $\text{SO}_2$  in DMF-TBAPF<sub>6</sub> (tetrabutylammonium hexafluorophosphate)<sup>6</sup> at  $-0.13\text{V}$  and  $+0.63\text{V}$  (vs.  $\text{AgCl}$  coated  $\text{Ag}$  wire), which were assigned to the oxidation of  $\text{SO}_2^-$  and  $\text{S}_2\text{O}_4^{2-}$ .

Fouchard observed that the electrolysis of  $\text{SO}_2$  in DMF-TEAP gradually turned the solution from bright blue to red to colorless.<sup>7</sup> Raman spectra of a

<sup>4</sup>Magno, F., Mazzochin, G. A. and Bontempelli, G., "Voltammetric Behavior of Sulphur Dioxide at a Platinum Electrode in Dimethylformamide," Electroanalytical Chemistry and Interfacial Electrochemistry, Vol. 57, 1974, pp. 89-96.

<sup>5</sup>Kastening, B. and Gostisa-Mihelcic, B., "An ESR Investigation of the Complex Formation Between  $\text{SO}_2$  and Electrogenerated  $\text{SO}_2^-$ ," Journal of Electroanalytical Chemistry, Vol. 100, 1979, pp. 801-808.

<sup>2</sup>See footnote 2 on page 9.

<sup>6</sup>Bowden, W. L. and Dey, A. N., "Primary  $\text{Li}/\text{SOCl}_2$  Cells XI.  $\text{SOCl}_2$  Reduction Mechanism in a Supporting Electrolyte," Journal of the Electrochemical Society, Vol. 127, 1980, pp. 1419-1426.

<sup>7</sup>Fouchard, D. T., Gardner, C. L., Adams, W. A. and Laman, F. C., "Raman and ESR Spectroscopic Studies of the Electroreduction of Sulphur Dioxide," in Proceedings of the Symposium on Lithium Batteries, Electrochemical Society Meeting, Hollywood (FL), October, 1980, pp. 156-158.

completely electrolysed solution were characteristic of the dithionite ion. ESR spectra were used to estimate the equilibrium constant for eqn. 1 as  $600 \text{ M}^{-1}$ . In addition to the anions already identified,  $\text{SO}_2^-$  and  $\text{SO}_2\text{SO}_2^-$ , a third was proposed:



2. Mercury Electrode. Gardner et al initiated a study of the effects of solvent and electrolyte on the distribution of products<sup>8</sup> among  $\text{SO}_2^-$ ,  $\text{SO}_2\text{SO}_2^-$ , and  $\text{S}_2\text{O}_4^{2-}$ . Most of the reported results were obtained in DMF. Two anodic cyclic voltammetry peaks, two ESR peaks and two pulse polarographic oxidations were observed in DMF-TEAP, which were attributed to  $\text{SO}_2^-$  (-1.17V vs. Ag/AgNO<sub>3</sub>) and  $\text{SO}_2\text{SO}_2^-$  (-0.65V). The equilibrium constant for formation of the complex,  $\text{SO}_2\text{SO}_2^-$ , was calculated to be  $4360 \text{ M}^{-1}$ .

#### B. ALKALI SALTS.

1. Mercury Electrode. The reduction of  $\text{SO}_2$  in DMF-LiClO<sub>4</sub> was shown by Gardner et al to be almost completely irreversible<sup>8</sup> with an entirely different product, as evidenced by the potential of the single anodic oxidation peak in cyclic voltammetry (-0.61V). Several alkali perchlorates were studied, with the lithium salt producing dithionite and the potassium salt producing the complex,  $\text{SO}_2\text{SO}_2^-$ .

<sup>8</sup>Gardner, C. L., Fouchard, D. T., Laman, F. C. and Fawcett, W. R., "The Kinetics and Mechanism of the Reduction of Sulphur Dioxide in Nonaqueous Media," in Proceedings of the Symposium on Lithium Batteries, Electrochemical Society Meeting, Los Angeles, October, 1979, pp. 545-559.

## Chapter 3

## DIMETHYLSULFOXIDE (DMSO)

I. CHEMICAL REDUCTION

Rinker and Lynn's solution of Na(Hg) and SO<sub>2</sub> in DMSO changed color from blue to purple to black to violet to red, finally resulting in a white precipitate.<sup>1</sup> The formation of the blue radical ion (SO<sub>2</sub>SO<sub>2</sub><sup>-</sup>) occurred much faster than in DMF. The nature of the red radical ion (RRI) was not clear until experiments had been run in formamide (see Chapter 6). The white precipitate, shown to be chiefly sodium dithionite, also formed much faster than in DMF.

II. ELECTROCHEMICAL INVESTIGATIONA. TETRAETHYLAMMONIUM SALTS.

1. Platinum Electrode. Bonnaterre and Cauquis observed that the reduction potential of SO<sub>2</sub> in DMSO-TEAP varied with the concentration of SO<sub>2</sub>, with a sharp change in the behavior occurring at about 10<sup>-2</sup>M.<sup>9</sup> A dimerization, as written in equation 2, resulting in a coating of dithionite on the electrode surface, was used to explain anomalous results. The ratio of the anodic to cathodic peaks from cyclic voltammetry decreased as the SO<sub>2</sub> concentration increased, as well as when the scan rate was increased. This decrease followed the predictions of Olmstead, Hamilton and Nicholson for a dimerization following electron transfer.<sup>10</sup> The change of reduction potential with the concentration of SO<sub>2</sub> agreed with Laviron's observation that this was characteristic of diffusion controlled electron transfer followed by dimerization.<sup>11</sup> The weak EPR signal attributed to SO<sub>2</sub><sup>-</sup> indicated that the equilibrium was largely shifted toward the dimer.

<sup>1</sup>See footnote 1 on page 9.

<sup>9</sup>Bonnaterre, R. and Cauquis, G., "Dimerization Consécutive a un Transfert Monoélectronique II. Réduction Electrochimique du Bioxyde de Soufre dans le Diméthyl Sulfoxyde," Electroanalytical Chemistry and Interfacial Electrochemistry, Vol. 32, 1971, pp. 215-223.

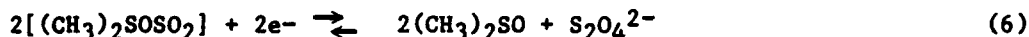
<sup>10</sup>Olmstead, M. L., Hamilton, R. G. and Nicholson, R. S., "Theory of Cyclic Voltammetry for a Dimerization Reaction Initiated Electrochemically," Analytical Chemistry, Vol. 41, 1969, pp. 260-267.

<sup>11</sup>Laviron, E., "Mechanism of the Polarographic Reduction of Aromatic Carbonyl Derivatives: Influence of Dimerization of the Free Radical Formed in the First Reduction Stage," Collection of Czechoslovak Chemical Communications, Vol. 30, 1965, pp. 4219-4236.

2. Mercury Electrode. Dehn et al obtained a polarographic wave for  $\text{SO}_2$  in DMSO-TEAP at  $-0.77\text{V}$  (vs. aq. SCE),<sup>12</sup> observing that the potential of the wave depended on the amount of water in the solution. The extensive solubility of  $\text{SO}_2$  in DMSO was explained by the formation of the complex



which could be reduced in the following manner:



#### B. LITHIUM SALTS.

1. Mercury Electrode. Differential pulse polarography was investigated by Garber and Wilson as a means of analysis of  $\text{SO}_2$  in air.<sup>13</sup> Garber's samples were bubbled through DMSO-LiCl, deaerated and analyzed. The sensitivity was sufficient, with the resultant peak heights proportional to  $\text{SO}_2$  concentration, up to at least millimolar concentrations. Interferences were found from nitrogen oxide and with water concentrations greater than 5%.

Bruno et al sought to evaluate Garber and Wilson's method, finding that nitrogen oxides did not interfere and could be analyzed simultaneously.<sup>14</sup> The half-wave potential was  $-0.875\text{V}$  (vs. calomel in DMSO-0.1 M LiCl).

Bruno, Caselli and Traini also studied the cyclic voltammetric behavior of  $\text{SO}_2$  in DMSO-LiNO<sub>3</sub>.<sup>15</sup> The three anodic peaks were assigned to the oxidation of  $\text{SO}_2^-$  resulting from the monomerization of  $\text{S}_2\text{O}_4^{2-}$  ( $-0.67\text{V}$  vs. calomel in DMSO-0.1M LiCl), the direct oxidation of dithionite ( $-0.54\text{V}$ ) and the oxidation of the complex,  $\text{SO}_2\text{S}_2\text{O}_4^{2-}$  ( $-0.22\text{V}$ ). After complete electrolysis, a fourth anodic wave appeared which could have been due to the oxidation of  $\text{SO}_2^{2-}$  obtained from the disproportionation reaction:



A solution of  $\text{SO}_2$  was electrolysed on a Hg pool at  $-1.0\text{V}$  (vs. SCE), with the amount of unreduced  $\text{SO}_2$  monitored by voltammetry. When the electrolysis was stopped at less than 300s, the original  $\text{SO}_2$  wave could be regenerated by

<sup>12</sup>Dehn, H., Gutmann, V., Kirch, H. and Schober, G., "Gaspolarographie," Monatshefte Chemie, Vol. 93, 1962, pp. 1348-1352.

<sup>13</sup>Garber, R. W. and Wilson, C. E., "Determination of Atmospheric Sulfur Dioxide by Differential Pulse Polarography," Analytical Chemistry, Vol. 44, 1972, pp. 1357-1360.

<sup>14</sup>Bruno, P., Caselli, M., DellaMonica, M. and DiFano, A., "Simultaneous Determination of  $\text{SO}_2$ , NO and  $\text{NO}_2$  in Air by Differential Pulse Polarography," Talanta, Vol. 26, 1979, pp. 1011-1014.

<sup>15</sup>Bruno, P., Caselli, M. and Traini, A., "Study of Sulfur Dioxide Reduction Mechanism in Dimethyl Sulfoxide," Journal of Electroanalytical Chemistry, Vol. 113, 1980, pp. 99-111.

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oxidation at  $-0.150\text{V}$ , but only after times exceeding  $700\text{s}$ . When the electrolysis was allowed to proceed longer than  $300\text{s}$ , it was impossible to regain all of the original  $\text{SO}_2$  by reoxidation. The effect of changing the anion of the supporting electrolyte was also noted, with  $E_{1/2}$  for  $\text{SO}_2$  found to be  $-0.711\text{V}$  in  $0.1\text{M LiNO}_3$ ,  $-0.736\text{V}$  in  $\text{LiCl}$  and  $-0.710\text{V}$  in  $\text{LiClO}_4$ .

## Chapter 4

## ACETONITRILE (AN)

I. ELECTROCHEMICAL INVESTIGATIONA. TETRAALKYLAMMONIUM SALTS.

1. Platinum Electrode. Bowden and Dey found no evidence for the reoxidation of  $\text{SO}_2^-$  in AN-TBAPF<sub>6</sub><sup>6</sup> and assigned the single anodic peak obtained by CV (-0.3V vs. AgCl coated Ag wire) to the oxidation of dithionite,  $\text{S}_2\text{O}_4^{2-}$ .

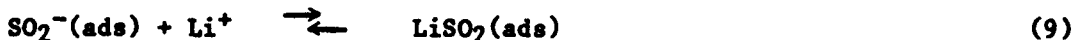
2. Mercury Electrode. The  $E_{1/2}$  for  $\text{SO}_2$  in AN-TEAP was found by Gardner et al to be -1.080V (vs. Ag/AgNO<sub>3</sub>).<sup>8</sup> The equilibrium constant for equation 1 was calculated to be  $18470 \text{ M}^{-1}$ , indicating much more extensive complex formation than in DMF.

B. LITHIUM SALTS.

1. Platinum Electrode. Geronov, Moshtev and Puresheva reported one anodic peak appearing during CV in AN-LiBr, but only at  $\text{SO}_2$  concentrations greater than 0.1M.<sup>16</sup> This peak (+0.17V vs. SCE) was proposed to be due to oxidation of a product adsorbed onto the surface of the electrode as a result of the reactions:



and



rather than to oxidation of dissolved species from the bulk of the solution.  $\text{SO}_2$  was regenerated from the oxidation occurring at +0.17V, as demonstrated by repeated cycles in the ranges 0V to -0.7V and +0.4V to -0.7V. Lithium deposition was observed to occur at potentials more negative than -1.5V and

<sup>6</sup>See footnote 6 on page 10.

<sup>8</sup>See footnote 8 on page 11.

<sup>16</sup>Geronov, Y., Moshtev, R. V. and Puresheva, B., "Electrochemical Reduction of Sulphur Dioxide on Inert Electrodes in Acetonitrile Solutions," Journal of Electroanalytical Chemistry, Vol. 108, 1980, pp. 335-346.

bromide oxidation at potentials more positive than +0.6V. The reduction potential for  $\text{SO}_2$  changed linearly with the logarithm of the scan rate, as predicted by Srinivasan and Gileadi for slow electrochemical adsorption processes.<sup>17</sup> Calculation of the associated electric charge showed that the electrode surface was being covered by a monolayer of product.

2. Glassy Carbon Electrode. The electric charge calculated by Geronov et al for glassy carbon was approximately twice that for platinum, presumably due to differences in the electrode surfaces.<sup>16</sup> The ratio of the anodic peak to the cathodic peak was larger for GC than for Pt, possibly due to different bonding energies between the adsorbed coating and the substrates.

<sup>17</sup>Srinivasan, S. and Gileadi, E., "The Potential Sweep Method: A Theoretical Analysis," Electrochimica Acta, Vol. 11, 1966, pp. 321-335.

<sup>16</sup>See footnote 16 on page 17.



## Chapter 5

## PROPYLENE CARBONATE (PC)

I. ELECTROCHEMICAL INVESTIGATIONA. LITHIUM SALTS.

1. Platinum Electrode. Tikhonova et al observed one anodic peak during CV in PC-LiClO<sub>4</sub> (+0.525V vs. TlCl in PC)<sup>18</sup> which was assigned to the oxidation of anion radicals which have not yet reacted according to the scheme:



The insoluble lithium dithionite coated the electrode surface, blocking further reaction. On repeated cycles, the peaks were greatly diminished.

Shembel' et al found two anodic peaks during CV of a similar PC-LiClO<sub>4</sub> solution containing about 20 times as much SO<sub>2</sub> (2.2M vs. 0.12M).<sup>19</sup> These peaks were attributed to the oxidation of SO<sub>2</sub><sup>-</sup> (3.42V vs. Li) and S<sub>2</sub>O<sub>4</sub><sup>2-</sup> (4.08V). Blockage of the electrode surface by product buildup was noted, but with the additional observation that at low sweep rates (10mV/s), during repeated scans, the cathodic peak increased from cycle to cycle. When the reduction product was completely reoxidized (i.e., both anodic peaks were traversed in the scan), the system could be operated in reverse. The anodic peak became more positive as the switching potential became more negative and the potential difference between the cathodic and anodic peaks increased (indicating increased overpotential). An SO<sub>2</sub> - solvent complex was also postulated to explain lower than expected cathodic currents.

2. Glassy Carbon Electrode. Shembel' et al observed only one anodic peak on glassy carbon, as opposed to two on platinum.<sup>19</sup> The anodic peak grew, the more negative the switching potential. Lithium was deposited at negative potentials, as indicated by an anodic dissolution peak.

<sup>18</sup>Tikhonova, L. S., Kurchashova, N. A., Raikhel'son, L. B., Nikol'skii, V. A. and Sokolov, L. A., "Investigation of the Electrochemical Reduction of Sulfur Dioxide in Propylene Carbonate," Soviet Electrochemistry, Vol. 14, 1978, pp. 1563-1566.

<sup>19</sup>Shembel', E. M., Litvinova, V. I., Maksyuta, I. M., Moskovskii, V. Z., Sokolov, L. A., and Ksenzhek, O. S., "Cathodic Reduction of Sulfur Dioxide in Nonaqueous Electrolytes: Lithium Perchlorate Solution in Propylene Carbonate," Soviet Electrochemistry, Vol. 15, 1979, pp. 1671-1677.

## Chapter 6

## OTHER SOLVENTS

I. FORMAMIDEA. CHEMICAL REDUCTION.

Rinker and Lynn observed that when sodium amalgam was added to a solution of  $\text{SO}_2$  in formamide, a red intermediate (RRI) quickly developed, just as quickly becoming colorless.<sup>1</sup> When DMF was added to RRI, blue radical ion (BRI) appeared. Apparently both had the formula,  $\text{SO}_2\text{SO}_2^-$ , with color differences due to changes in solvation. The colorless ion (CI) appeared to be  $\text{SO}_2\text{SO}_2^{2-}$ . A solution of CI could be changed to RRI by adding  $\text{SO}_2$ . Addition of  $\text{SO}_2$  to sodium dithionite dissolved in formamide resulted in RRI. When RRI was further reduced by  $\text{Na}(\text{Hg})$ , CI was formed. This series of reversible reactions demonstrated the chemical relationships among the species.

II. HEXAMETHYLPHOSPHORAMIDE (HMPA)A. ELECTROCHEMICAL INVESTIGATION.1. Tetraethylammonium Salts.

a. MERCURY ELECTRODE. The  $E_{1/2}$  for  $\text{SO}_2$  in HMPA-TEAP was found by Gardner et al to be  $-1.167\text{V}$  (vs.  $\text{Ag}/\text{AgNO}_3$ ), with the equilibrium constant for equation 1 equal to  $1456\text{M}^{-1}$ . This indicated considerably less stability of the complex in HMPA.<sup>8</sup>

III. METHYLENE CHLORIDEA. ELECTROCHEMICAL INVESTIGATION.1. Tetraalkylammonium Salts.

a. PLATINUM ELECTRODE. Bowden and Dey found in  $\text{MeCl}_2\text{-TBAPF}_6$  that CV of  $\text{SO}_2$  resulted in two anodic peaks, assigned to the reduction products,  $\text{SO}_2^-$  ( $-0.4\text{V}$  vs.  $\text{AgCl}$  coated  $\text{Ag}$  wire) and  $\text{S}_2\text{O}_4^{2-}$  ( $+0.06\text{V}$ ).<sup>6</sup>

<sup>1</sup>See footnote 1 on page 9.

<sup>8</sup>See footnote 8 on page 11.

<sup>6</sup>See footnote 6 on page 10.

## Chapter 7

## DISCUSSION

The reduction of  $\text{SO}_2$  in nonaqueous solvents results in two major products:  $(\text{SO}_2)_x\text{SO}_2^-$  and  $\text{S}_2\text{O}_4^{2-}$ . Some disagreement exists, as shown in Tables 4 and 5, but the predominant species depends on numerous factors, including the nature of the solvent, the supporting electrolyte,  $\text{SO}_2$  concentration, temperature, electrode surface and the presence of impurities such as water.

1. SOLVENT. All of the solvents studied were polar and aprotic. Differences in the observed mechanism for  $\text{SO}_2$  reduction seem to be directly related to individual capacities for solvation. Baranski and Fawcett found that when the solvent was changed, keeping a fixed supporting electrolyte, the log of the standard rate constant for the reduction of  $\text{Na}^+$  ions at a Hg electrode varied linearly with free energies of solvation.<sup>20</sup> Gardner et al demonstrated that the products of reduction depend on the degree of ionic association between the free radical and supporting electrolyte cations.<sup>8</sup> Polar solvents of high dielectric constant discourage ion pairing, because of stronger solute-solvent interactions.<sup>21</sup> The solvents in these studies are all highly polar, but the dielectric constants vary considerably, as shown by Covington's<sup>21</sup> values in Table 6.

In poor solvators, the free radical ion is more available for complexation by unreduced  $\text{SO}_2$  to form the species,  $(\text{SO}_2)_x\text{SO}_2^-$ , demonstrated by Gardner et al with their values for the complex formation constant of  $1456\text{M}^{-1}$  in HMPA, an excellent solvator,  $4363\text{M}^{-1}$  in DMF and  $18470\text{M}^{-1}$  in AN<sup>8</sup>, presented with other reported values in Table 7. Also observed by Gardner et al was a shift in half wave potential, from -1.257 in DMF to -1.167 in HMPA to -1.080 in AN. This transition does not follow the trend of complex formation attributed to solvation.

<sup>20</sup>Baranski, A. and Fawcett, W. R., "Medium Effects in the Electroreduction of Alkali Metal Cations," Journal of Electroanalytical Chemistry, Vol. 94, 1978, pp. 237-240.

<sup>8</sup>See footnote 8 on page 11.

<sup>21</sup>Covington, A. K. and Dickinson, T., Ed., Physical Chemistry of Organic Solvent Systems (London: Plenum Press, 1973), pp. 332-393.

Color differences have been observed in solutions of reduced  $\text{SO}_2$ . Some of this effect can be attributed to differences in solvation mechanisms. Rinker and Lynn found that amides with one or more protons on the amide nitrogen gave a red intermediate, where others gave a blue species.<sup>1</sup> Dry DMF is aprotic and nonbasic, but other such solvents, e.g. dioxane, cannot stabilize BRI. The unexpected stability of BRI in DMF was explained by the absence of  $\text{H}^+$  and  $\text{OH}^-$ , the solvent "cage" effects resulting from complexes between solvent and radical, and resonance structures.

An equilibrium constant was calculated for the dimerization of  $\text{SO}_2^-$  in DMSO<sup>15</sup> to be  $10^5$ , as opposed to 24 in DMF<sup>8</sup>.

It would seem that generally AN favors complex formation, whereas DMSO favors dimerization.

2. SUPPORTING ELECTROLYTE. Studies by Gardner et al showed that the formation constant for the complex varied when the supporting electrolyte was changed.<sup>8</sup> In DMF, decreasing the cation size from  $\text{K}^+$  to  $\text{Na}^+$  to  $\text{Li}^+$  resulted in increasing dimer formation. It was concluded that the much larger tetraalkylammonium salts favor complexation, while lithium salts favor dimerization.

Interesting comparisons can be made, however, when examining Table 4. Both Martin<sup>3</sup> and Gardner et al<sup>8</sup> reported two anodic peaks in DMF-0.1M TEAP separated by 0.5V, assigned to the oxidation of  $\text{SO}_2^-$  and  $\text{SO}_2\text{SO}_2^-$ . Magno et al<sup>4</sup> and Bowden and Dey<sup>6</sup> found two anodic peaks in DMF-TBA<sup>+</sup> separated by 0.75V which were attributed to the oxidation of  $\text{SO}_2^-$  and  $\text{S}_2\text{O}_4^{2-}$ . Magno et al observed the complex spectrophotometrically, but reasoned that it was too unstable to be detected voltammetrically. It would seem that different species are responsible for the peaks observed with TEA<sup>+</sup> and TBA<sup>+</sup>, as evidenced by the different voltage separations.

Bruno et al found a shift in the  $\text{SO}_2$  reduction potential when the anion was changed in a series of  $\text{Li}^+$  salts.<sup>15</sup> If complexation of  $\text{SO}_2$  by the anion had been responsible, a cathodic shift would have occurred on increasing the electrolyte concentration. It was proposed that changing the anion modified the rate of dimerization. The observed half-wave potential was plotted

<sup>1</sup>See footnote 1 on page 9.

<sup>15</sup>See footnote 15 on page 14.

<sup>8</sup>See footnote 8 on page 11.

<sup>3</sup>See footnote 3 on page 9.

<sup>4</sup>See footnote 4 on page 10.

<sup>6</sup>See footnote 6 on page 10.

vs.  $\psi_0$ , the potential at the outer Helmholtz plane, for different concentrations of  $\text{LiClO}_4$  and  $\text{LiNO}_3$ , resulting in reasonably linear correlations.

3. CONCENTRATION OF  $\text{SO}_2$ . Geronov et al reported that anodic peaks did not appear in cyclic voltammograms until the  $\text{SO}_2$  concentration was at least  $0.1\text{M}$ <sup>16</sup>, but many other studies observed peaks at concentrations in the range of  $10^{-4}$  to  $10^{-2}\text{M}$ .

Gardner et al found a trend toward more anodic potentials for the half-wave potential of  $\text{SO}_2$  in DMF-TEAP<sup>8</sup>, as shown in Table 8. On the other hand, Bruno et al<sup>15</sup> and Martin and Sawyer<sup>3</sup> reported that the peak potential shifted cathodic as  $[\text{SO}_2]$  increased. In a detailed study, Bonnaterre and Cauquis observed that the peak potential became more anodic as the concentration of  $\text{SO}_2$  increased<sup>9</sup>, until the effect reversed at a concentration between  $10^{-3}$  and  $10^{-2}\text{M}$  (depending on the sweep rate) and the potential moved toward more cathodic potentials with continued increase in  $\text{SO}_2$ .

As the amount of  $\text{SO}_2$  increased, the ratio of the more negative anodic peak to the more positive anodic peak decreased, as observed by Magno et al<sup>4</sup> and Martin and Sawyer<sup>3</sup> in DMF and Bonnaterre and Cauquis in DMSO<sup>9</sup>. This fact could be taken as evidence for the assignment of the second anodic peak to the oxidation of the complex,  $(\text{SO}_2)_x\text{SO}_2^-$ .

4. TEMPERATURE. Magno et al found a strong dependence of the potentials of the anodic peaks on temperature.<sup>4</sup> At  $0^\circ\text{C}$  the peaks were at  $-0.5$  and  $+0.2\text{V}$  (vs. SCE), but at  $45^\circ\text{C}$  they shifted cathodically to  $-0.8$  and  $-0.25\text{V}$ . The cathodic peak potential was practically unchanged. The ratio of the anodic peaks decreased as the temperature decreased.

Gardner et al reported that the shift observed in the reduction potential of  $\text{SO}_2$  depended on the nature of the electrolyte<sup>8</sup>, as shown in Table 9. In DMF-TEAP, the potential became more positive at lowered temperature.

According to Bonnaterre and Cauquis, increased temperature ( $55^\circ\text{C}$ ) reduced the effect of the dimer coating on further reactions at the electrode surface<sup>9</sup>, making the results more reproducible and less affected by other parameters.

5. ELECTRODE SURFACE. Martin and Sawyer reported that cyclic voltammograms of  $\text{SO}_2$  in DMF-TEAP obtained on Pt and Au electrodes are similar,

<sup>16</sup>See footnote 16 on page 17.

<sup>8</sup>See footnote 8 on page 11.

<sup>15</sup>See footnote 15 on page 14.

<sup>3</sup>See footnote 3 on page 9.

<sup>9</sup>See footnote 9 on page 13.

<sup>4</sup>See footnote 4 on page 10.

but the ratio of the anodic peak to the cathodic peak is larger at Pt<sup>3</sup>. It was also pointed out that the Au electrode is less susceptible to hysteresis. Gardner et al ran cyclic voltammetry in the same DMF-TEAP solution at the Hg electrode (HMDE) and observed analogous results<sup>8</sup>, as can be seen in Table 4. Geronov et al studied the anodic electric charge for Pt and GC electrodes, finding it to be much lower for Pt, presumably due to the relative smoothness of the surface.<sup>16</sup> The GC surface was more rapidly passivated, as demonstrated by repeated scans. Only one anodic peak was observed on GC by Shembel' et al, compared to two on Pt.<sup>19</sup>

6. EFFECT OF WATER. Tikhonova et al added water to the PC-LiClO<sub>4</sub> electrolyte, increasing the reduction peak and producing a second reduction peak at more negative potentials.<sup>18</sup> Geronov et al concluded that the effect of water was not evident immediately, but appeared gradually over a period of hours as the cathodic peak increased.<sup>16</sup>

Dehn et al had found that small amounts of water increased the half-wave potential of SO<sub>2</sub> in DMSO, whereas the presence of greater than 5 vol % split the wave into two adjacent waves.<sup>12</sup>

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<sup>3</sup>See footnote 3 on page 9.

<sup>8</sup>See footnote 8 on page 11.

<sup>16</sup>See footnote 16 on page 17.

<sup>19</sup>See footnote 19 on page 19.

<sup>18</sup>See footnote 18 on page 19.

<sup>16</sup>See footnote 16 on page 17.

<sup>12</sup>See footnote 12 on page 14.

## Chapter 8

## SUMMARY AND PLANS

As the previous discussion showed, there has been no general agreement on the mechanism of the reduction of  $\text{SO}_2$  in nonaqueous solvents. The choice of solvent affects the outcome of the reduction, with DMF and AN favoring the complex and DMSO the dimer. Electrolytes with large cations favor the complex, but  $\text{Li}^+$  ions produce the dimer. This generalization is questionable in view of the discrepancies reported between studies in  $\text{TEA}^+$  and  $\text{TBA}^+$  solutions (see Chapter 7, section 2). Electrode surface is also important because of the possibilities of catalytic effects and/or side reactions.

Cyclic Voltammetry generates information about reaction reversibility, intermediate species and reduction mechanisms. The effect of changes in electrolyte and electrode surface is observed in the position and shape of voltammetric peaks.

Coulometry determines the number of electrons involved in the electron transfer, possibly revealing mechanistic information in the shape of the current-time curve.

Controlled potential electrolysis produces reactive intermediates which can be detected by other voltammetric techniques or by UV-vis spectroscopy, which monitors the appearance and disappearance of charge-transfer type complexes during the course of the reduction. Those species which have an unpaired electron are also detectable with ESR spectroscopy.

Rotating ring-disc electrodes provide information about the half-life of soluble intermediates, possibly detecting adsorption at the electrode surface.

More detailed experimental plans will be presented in Part II of this report, along with preliminary results from cyclic voltammetry and other studies.

TABLE 1 PUBLISHED STUDIES OF SO<sub>2</sub> REDUCTION\*

<u>AUTHOR</u>	<u>PUBLICATION DATE</u>	<u>SOLVENT</u>	<u>ELECTROLYTE</u>	<u>WORKING ELECTRODE</u>
DEHN	1962	DMSO	TEAP	Hg
DINSE	1968	DMF	TPAP, TBAI	Pt
RINKER**	1968	DMF, DMSO, F	----	---
BONNATERRE	1971	DMSO	TEAP	Pt
GARBER	1972	DMSO	LiCl	Hg
MARTIN	1972	DMF	TEAP	Pt
MARTIN	1973	DMF	TEAP	Pt
MAGNO	1974	DMF	TBAP	Pt
TIKHONOVA	1978	PC	LiClO <sub>4</sub>	Pt
BRUNO	1979	DMSO	LiCl	Hg
KASTENING	1979	DMF	TEABr	Pt
SHEMBEL'	1979	PC	LiClO <sub>4</sub>	Pt, GC
GARDNER	1979	DMF, AN, HMPA	TEAP, LiClO <sub>4</sub>	Hg
GERONOV	1980	AN	LiBr	Pt, GC
BOWDEN	1980	DMF, AN, MeCl <sub>2</sub>	TBAPF <sub>6</sub>	Pt
BRUNO	1980	DMSO	LiCl, LiNO <sub>3</sub> , LiClO <sub>4</sub>	Hg
FOUCHARD	1980	DMF	TEAP	Pt

\* ABBREVIATIONS EXPLAINED IN TEXT

\*\* CHEMICAL REDUCTION WITH Na(Hg)



TABLE 2 CYCLIC VOLTAMMETRY STUDIES

<u>AUTHOR</u>	<u>SOLVENT</u>	<u>ELECTROLYTE</u>	<u>ELECTRODE</u>	<u>SCAN RATE</u>	<u>[SO<sub>2</sub>]</u>	<u>REFERENCE ELECTRODE</u>	<u>REDUCTION POTENTIAL</u>	<u>OXIDATION POTENTIALS</u>
MARTIN	DMF	0.1M TEAP	Pt	100	5x10 <sup>-3</sup>	SCE	-0.84, -1.65	-0.74, -0.25
MAGNO	DMF	0.1M TEAP	Pt	200	4.25x10 <sup>-3</sup>	SCE	-0.95	-0.65, +0.1
BOWDEN	DMF	TEAPF <sub>6</sub>	Pt	200	?	AgCl coated Ag wire	-0.8	+0.4, +0.63
GARDNER	DMF	0.1M TEAP	Hg	200	10 <sup>-2</sup>	Ag/.05M AgNO <sub>3</sub> -.05M TEAP in DMSO	-1.3	-1.17, -0.65
GARDNER	DMF	0.1M LiClO <sub>4</sub>	Hg	200	10 <sup>-3</sup>	"	-1.325	-0.61
BRUNO	DMSO	0.5M LiNO <sub>3</sub>	Hg	50	1.8x10 <sup>-4</sup>	Hg <sub>2</sub> Cl <sub>2</sub> in 0.1M LiCl in DMSO	-0.73	-0.67, -0.54, -0.22
BOWDEN	AN	TEAPF <sub>6</sub>	Pt	1000	?	AgCl coated Ag wire	-1.3	-0.3
GERONOV	AN	0.1M LiBr	Pt	280	0.96	SCE	-0.35	+0.17
GERONOV	AN	0.1M LiBr	GC	280	0.96	SCE	-0.33	+0.33
TIKHONOVA	PC	1M LiClO <sub>4</sub>	Pt	80	0.12	TiCl in PC	-0.1	+0.525
SHEBEL'	PC	1M LiClO <sub>4</sub>	Pt	40	2.2	Li	+2.64	+3.42 +4.08
BOWDEN	MeCl <sub>2</sub>	TEAPF <sub>6</sub>	Pt	100	?	AgCl coated Ag wire	-1.1	-0.4 +0.06

TABLE 3 OTHER VOLTAMMETRIC STUDIES

AUTHOR	SOLVENT	ELECTROLYTE	ELECTRODE	TECHNIQUE*	REFERENCE ELECTRODE	[SO <sub>2</sub> ]	POTENTIAL
GARDNER	DMF	0.1M TEAP	Hg	DCP	Ag/.05M AgNO <sub>3</sub> -.05M TEAP in DMF	5x10 <sup>-4</sup>	-1.279
GARDNER	DMF	0.1M TEAP	Hg	DCP	"	10 <sup>-2</sup>	-1.257
GARDNER	DMF	0.1M TEAP	Hg	DCP	"	5x10 <sup>-3</sup>	-1.250
BONNATERRE	DMSO	0.1M TEAP	Pt	RDV	Ag/10 <sup>-3</sup> M AgCl <sub>2</sub> -10 <sup>-1</sup> M LiCl	10 <sup>-3</sup>	-0.41
DEHN	DMSO	TEAP	Hg	DCP	SCE	?	-0.77
GARBER	DMSO	0.1M LiCl	Hg	DPP	Ag/AgCl in 0.1M LiCl in DMSO	1.1x10 <sup>-3</sup>	-0.737
BRUNO	DMSO	0.1M LiCl	Hg	DPP	Hg <sub>2</sub> Cl <sub>2</sub> in 0.1M LiCl in DMSO	4.4x10 <sup>-5</sup>	-0.875
BRUNO	DMSO	0.1M LiNO <sub>3</sub>	Hg	DCP	"	1.0x10 <sup>-4</sup>	-0.711
BRUNO	DMSO	0.1M LiCl	Hg	DCP	"	1.0x10 <sup>-4</sup>	-0.736
BRUNO	DMSO	0.1M LiClO <sub>4</sub>	Hg	DCP	"	1.0x10 <sup>-4</sup>	-0.710
GARDNER	AN	0.1M TEAP	Hg	DCP	Ag/.05M AgNO <sub>3</sub> -.05M TEAP in DMF	?	-1.080
GARDNER	HMPA	0.1M TEAP	Hg	DCP	"	?	-1.167

\*DCP = DC Polarography

RDV = Rotating Disc Voltammetry

DPP = Differential Pulse Polarography

TABLE 4 ASSIGNMENT OF ANODIC PEAKS IN CYCLIC VOLTAMMETRY IN  
TETRAALKYLAMMONIUM SALT SOLUTIONS

<u>AUTHOR</u>	<u>SOLVENT</u>	<u>ELECTROLYTE</u>	<u>ANODIC PEAK POTENTIAL</u>	<u>SPECIES</u>	<u>ELECTRODE</u>
MARTIN	DMF	TEAP	-0.74	$\text{SO}_2^-$	Pt
			-0.24	$\text{SO}_2\text{SO}_2^-$	Pt
MAGNO	DMF	TBAP	-0.65	$\text{SO}_2^-$	Pt
			+0.1	$\text{S}_2\text{O}_4^{2-}$	Pt
BOWDEN	DMF	$\text{TBAPF}_6$	-0.13	$\text{SO}_2^-$	Pt
			+0.63	$\text{S}_2\text{O}_4^{2-}$	Pt
GARDNER	DMF	TEAP	-1.17	$\text{SO}_2^-$	Hg
			-0.65	$\text{SO}_2\text{SO}_2^-$	Hg
BONNATERRE	DMSO	TEAP		$\text{S}_2\text{O}_4^{2-}$	Pt
BOWDEN	AN	$\text{TBAPF}_6$	-0.3	$\text{S}_2\text{O}_4^{2-}$	Pt
BOWDEN	$\text{MeCl}_2$	$\text{TBAPF}_6$	-0.4	$\text{SO}_2^-$	Pt
			+0.06	$\text{S}_2\text{O}_4^{2-}$	Pt

TABLE 5 ASSIGNMENT OF ANODIC PEAKS IN CYCLIC VOLTAMMETRY IN ALKALI SALT SOLUTIONS

<u>AUTHOR</u>	<u>SOLVENT</u>	<u>ELECTROLYTE</u>	<u>ANODIC PEAK POTENTIAL</u>	<u>SPECIES</u>	<u>ELECTRODE</u>
GARDNER	DMF	LiClO <sub>4</sub>	-0.62	S <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	Hg
GARDNER	DMF	KClO <sub>4</sub>	?	SO <sub>2</sub> SO <sub>2</sub> <sup>-</sup>	Hg
BRUNO	DMSO	LiNO <sub>3</sub>	-0.67	SO <sub>2</sub> <sup>-</sup>	Hg
			-0.54	S <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	Hg
			-0.22	SO <sub>2</sub> S <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	Hg
GERONOV	AN	LiBr	+0.17	LiSO <sub>2</sub>	Pt
GERONOV	AN	LiBr	?	LiSO <sub>2</sub>	GC
TIKHONOVA	PC	LiClO <sub>4</sub>	+0.525	SO <sub>2</sub> <sup>-</sup>	Pt
SHEMBEL'	PC	LiClO <sub>4</sub>	+3.42	SO <sub>2</sub> <sup>-</sup>	Pt
			+4.08	S <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	Pt

TABLE 6 DIELECTRIC CONSTANTS ( $\epsilon$ ) AND DIPOLE  
MOMENTS ( $\delta$ ) OF NONAQUEOUS SOLVENTS

<u>SOLVENT</u>	<u><math>\epsilon</math></u>	<u><math>\delta</math></u>
F	109.5	3.73
PC	64.4	4.98
DMSO	46.7	3.96
DMF	36.7	3.86
AN	36.0	3.92
HMPA	29.6	5.39

TABLE 7 EQUILIBRIUM CONSTANT FOR COMPLEX FORMATION

<u>SOLVENT</u>	<u>ELECTROLYTE</u>	<u>AUTHOR</u>	<u>K</u>
DMF	TPAP	DINSE	$1.3 \times 10^4 \text{ M}^{-2}$
DMF	TEABr	KASTENING	$230 \text{ M}^{-1}$
DMF	TPAP	DINSE RECALCULATED BY KASTENING	$65-200 \text{ M}^{-1}$
DMF	TEAP	FOUCHARD	$600 \text{ M}^{-1}$
DMF	TEAP	GARDNER	$4360 \text{ M}^{-1}$
AN	TEAP	GARDNER	$18470 \text{ M}^{-1}$
HMPA	TEAP	GARDNER	$1456 \text{ M}^{-1}$

TABLE 8 VARIATION OF  $E_{1/2}$  WITH  $[SO_2]$  IN DMF-TEAP

<u><math>[SO_2]</math></u>	<u><math>E_{1/2}</math></u>
$5 \times 10^{-4}$	-1.279
$10^{-3}$	-1.257
$5 \times 10^{-3}$	-1.250

TABLE 9 VARIATION OF  $E_{1/2}$  WITH TEMPERATURE

## A. DMF-TEAP

<u>°C</u>	<u><math>E_{1/2}</math></u>
-10	-1.224
0	-1.234
20	-1.254

B. DMF-LiC10<sub>4</sub>

<u>°C</u>	<u><math>E_{1/2}</math></u>
-10	-1.260
0	-1.250
20	-1.235



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